



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Hirohisa Tanaka

Appln. No.: 10/520,068

Group Art Unit: 1754

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Examiner: Timothy C. VANOH

For: METHOD FOR PRODUCING PEROVSKITE-TYPE COMPOSITE OXIDE

DECLARATION UNDER 37 C.F.R. § 1.132

United States Patent and Trademark Office
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

I, Hirohisa TANAKA, hereby declare and state:

THAT I am a citizen of Japan;

THAT I received a Doctor of Engineering Degree in Catalysis Chemistry from The University of Tokyo in July 16, 1998;

THAT I was employed by Daihatsu Motor Co., Ltd. of Ikeda from February 1, 1989, ultimately holding the position of Executive Technical Expert of the Advanced Research and Development Division, and that I engaged in the development and production of the METHOD FOR PRODUCING PEROVSKITE-TYPE COMPOSITE OXIDE claimed in the present application;

THAT I became a co-inventor of the above-identified application;

THAT the following experiments were conducted by myself;

EXPERIMENTS

(Example 1) $\text{La}_{1.00}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ [Alkoxide Method/ $\text{Pd}(\text{AcAc})_2$]

Initially, an alkoxide mixed solution was prepared by charging 43.6 g (0.100 mol) of lanthanum methoxypropylate $[\text{La}(\text{OCHMeCH}_2\text{OMe})_3]$, and 33.5 g (0.095 mol) of iron methoxypropylate $[\text{Fe}(\text{OCHMeCH}_2\text{OMe})_3]$, in a 1000-mL round-bottomed flask and dissolving them in 200 mL of toluene added thereto with stirring.

Separately, 1.52 g (0.005 mol) of palladium acetylacetonate $[\text{Pd}(\text{CH}_3\text{COCHCOCH}_3)_2]$ was dissolved in 200 mL of toluene to obtain an organometal salt solution, and the organometal salt solution was further added to the alkoxide mixed solution in the round-bottomed flask to obtain a homogenous mixed solution containing LaFePd . Next, 200 mL of deionized water was added dropwise to the round-bottomed flask over about fifteen minutes to form a viscous brown precipitate on hydrolysis.

After stirring at room temperature for two hours, toluene and water were distilled off under reduced pressure to obtain a precursor of the LaFePd composite oxide. The precursor was placed on a petri dish, subjected to forced-air drying at 60°C for twenty-four hours, subjected to heat treatment at 700°C in the atmosphere for one hour using an electric furnace to obtain a blackish brown powder. The X-ray powder diffraction analysis of the powder revealed that it was identified as a single crystal phase comprising a composite oxide having a perovskite structure of $\text{La}_{1.00}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{O}_3$. The powder was found to have a specific surface area of $17 \text{ m}^2/\text{g}$ and a Pd content in the composite oxide of 2.16% by mass.

(Comparative Example 1) $\text{La}_{1.00}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ [Alkoxide Method/ $\text{Pd}(\text{NO}_3)_2$]

Initially, an alkoxide mixed solution was prepared by charging 43.6 g (0.100 mol) of lanthanum methoxypropylate $[\text{La}(\text{OCHMeCH}_2\text{OMe})_3]$, and 33.5 g (0.095 mol) of iron methoxypropylate $[\text{Fe}(\text{OCHMeCH}_2\text{OMe})_3]$, in a 1000-mL round-bottomed flask and dissolving them in 200 mL of toluene added thereto with stirring.

Separately, after 12.24g (corresponding to 0.53 g (0.005 mol) of Pd) of an aqueous palladium nitrate solution having a Pd content of 4.347% by mass was diluted with 40 mL of deionized water, an aqueous sodium hydroxide having a concentration of 5% was subsequently added to the diluted solution to adjust to pH 6.4. The aqueous solution thus obtained was added dropwise to the round-bottomed flask over about fifteen minutes to form a viscous brown precipitate on hydrolysis.

Subsequently, a blackish brown powder was obtained by the procedure of Example 1. The X-ray powder diffraction analysis of the powder revealed that it was identified as a single crystal phase comprising a composite oxide having a perovskite structure of $\text{La}_{1.00}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{O}_3$. The powder was found to have a specific surface area of $5 \text{ m}^2/\text{g}$ and a Pd content in the composite oxide of 2.16% by mass.

(Activity Measurement)

1) Endurance test

Each catalyst powder was subjected to heat-treatment at 1000°C for seventy-two hours. Further, each catalyst powder was subjected to treatment at 600°C for fifteen minutes under a reduced atmosphere (flow rate: 5L/min) shown in Table 1.

2) 20% and 50% Purification temperatures and 400°C Purification rate

Each catalyst powder thus obtained was molded into a pellet having a size of 0.5 mm to 0.75 mm to prepare a test sample. The samples were placed in a model gas flow shown in Table 2. The gas temperature was raised from room temperature to 430°C at temperature rising speed of 20°C/min. The gas concentration was measured during the rise of temperature. The temperatures at which the purification rate of CO, THC, and NOx reached 20% and 50% were determined as 20% and 50% Purification temperatures, respectively. The purification rate of CO, THC, and NOx that reached 20% and 50% at 400°C was determined as a 400°C purification rate. In the measurement, the sample weight was 0.3 g and the flow rate was 2.25L/min. The results thus obtained are shown in Table 3.

Table 1

	CO	H ₂	CO ₂	N ₂
Concentration (%)	7.5	2.5	8.0	Balance

Table 2

	CO	H ₂	C ₃ H ₆	C ₃ H ₈	O ₂	NO	CO ₂
Concentration (ppm)	7000	2333	500	133	6700	1700	80000

Table 3

No.	Sample	20% Purification temperature (°C)			50% Purification temperature (°C)			400°C Purification rate (%)		
		THC	NOx	CO	THC	NOx	CO	THC	NOx	CO
Example 1	La _{1.02} Fe _{0.95} Pd _{0.05} Oxide Pd(AcAc) ₂	302	232	271	342	334	342	75.8	78	62.6
Comparative Example 1	La _{1.02} Fe _{0.95} Pd _{0.05} Oxide Pd Nitrate	344	328	283	411	421	not reached	45.2	43.6	43.8

(Rate of Solid solution)

1) Pretreatment

Each catalyst powder was subjected to oxidation treatment at 800°C for five minutes under the air. Then, each catalyst powder was subjected to reduction treatment at 800°C for five minutes under a reduced atmosphere (H₂: 2.5%, CO: 7.5% N₂: balance). Further, each catalyst powder was subjected to re-oxidation treatment at 800°C for five minutes under the air.

Rates of solid solution of each catalyst powder thus obtained in the oxidation treatment, reduction treatment, and re-oxidation treatment were measured using the following method.

2) Measurement of rate of solid solution

Each catalyst powder was dissolved in an aqueous 7 wt% hydrochloric acid solution and allowed to stand at room temperature for 20 hours, and then each solution was filtered through a filter having a pore size of $0.1 \mu\text{m}$.

An amount of Pd dissolved in the resulting filtrate was determined by inductively coupled plasma (ICP) atomic emission spectroscopy and quantitative analysis of Pd in the residue was carried out by the X-ray diffraction (XRD)- scanning electron microscopy (SEM) analytical method. The amount of solid solution of Pd was calculated from these results. The results are shown in Table 4.

In the above method, the residue was produced during dissolving the respective powders in an aqueous 7 wt% hydrochloric acid solution. However, since Pd constituting a solid solution in a perovskite-type crystal structure was dissolved, a proportion of Pd constituting a solid solution in a perovskite-type crystal structure could be determined by measuring a concentration of Pd in the solution.

Table 4

No.	Sample	Rate of Solid solution (%)		
		Oxidation	Reduction	Re-oxidation
Example 1	$\text{La}_{1.02}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{Oxide}$ $\text{Pd}(\text{AcAc})_2$	93	0	91
Comparative Example 1	$\text{La}_{1.02}\text{Fe}_{0.95}\text{Pd}_{0.05}\text{Oxide}$ Pd Nitrate	57	0	55

I, the undersigned, declare that all statements made herein on my knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, of both, under Section 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any issuing thereon.

Signed this 13 day of April 2007.

A handwritten signature in cursive script, reading "Hirohisa Tanaka". The signature is written in dark ink and is positioned above a horizontal line.

Hirohisa TANAKA